

Synthesis and Characterization of Fluorescent Acenequinones as Dyes for Guest–Host Liquid Crystal Displays

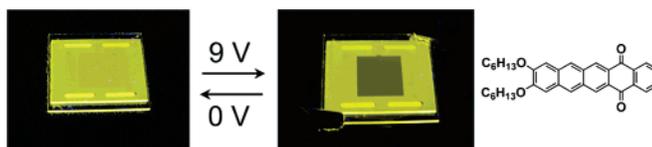
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ABSTRACT



Syntheses and spectroscopic properties of alkoxy-substituted *para*-acenequinones are reported. These compounds showed excellent alignment in nematic liquid crystals as evidenced by polarized UV–vis absorption and fluorescence measurements.

Guest–host liquid crystal displays (GH-LCDs) that use a LC/dye mixture as the active material have received much attention since their invention in the 1960s because of their wider viewing angle, daylight readability, and high stability in harsh environments.^{1–3} In GH-LCDs, the change in color intensity is obtained by controlling the direction of dichroic dye molecules which adsorb light more at one molecular axis than the others. The optimal parameters of GH-LCDs depend on the dichroic properties of dyes, their solubility in the LC host, and their stability under various environments. Anthraquinone and azo derivatives are the two major classes of dyes receiving the most intensive study.³

Recently, fluorescent dye based GH-LCDs, which combine the excellent hues and high brightness levels of emissive displays with the desirable features of LCDs, have been proposed as a less energy consuming display for portable electronics.^{4,5} For fluorescent dyes in LCs, the fluorescence intensity can be controlled in a way similar to absorption. Therefore, the development of fluorescent GH-LCDs requires synthesis of fluorescent dyes with a high dichroic ratio, a high quantum yield, and a strong emission in the visible

region. Additionally, the rodlike shape of nematic LC molecules favors alignment of elongated, rodlike dye molecules along the direction of the long molecular axis of nematic LC molecules.

In this study, we report emissive linear *para*-acenequinone dyes with large dichroic ratios in LC mixtures. We describe the syntheses of a group of alkoxy-substituted acenequinone derivatives, their solution absorption and emission spectra, and the polarized absorption and emission spectra of their LC solutions. These compounds demonstrated strong orientation properties and have excellent potential as fluorescent dyes for GH-LCDs.

Synthetic methodologies for preparing linear *para*-acenequinones have been previously reported,^{6–8} and the Diels–Alder (D–A) reaction between isobenzofurans (or their

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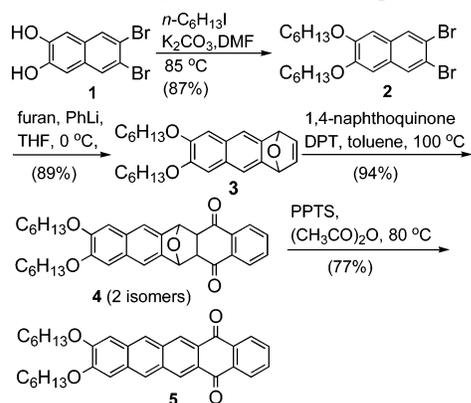
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analogues) and linear 1,4-quinones is one of the more efficient approaches.⁷ In this work, we employed 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPT) and anthracene 1,4-endoxide **3** to generate an isonaphthofuran, which is subsequently trapped by a quinone via a D–A mechanism.⁹ The D–A adducts are then easily converted into the corresponding acenequinones. This methodology avoids direct use of isobenzofuran/isonaphthofuran compounds, which are difficult to synthesize and are generally unstable. It has also allowed us to prepare various substituted acenequinones.

The synthetic route to a *para*-pentacenequinone is outlined in Scheme 1. The starting 6,7-dibromo-2,3-dihydroxynaphthalene (**1**), which was prepared from 2,3-dihydroxynaphthalene in two steps via a literature procedure,¹⁰ was converted to **2** by a Williamson ether synthesis. Intermediate **2** was treated with phenyllithium (PhLi) in the presence of excess furan, at low temperature, to produce **3**. The generation of **4** was successfully accomplished by treating **3** with DPT, in the presence of 1,4-naphthoquinone. Pentacenequinone **5** was then obtained from dehydration of **4**, which could be realized by employing acetic acid,^{9b} *p*-toluenesulfonic acid (*p*-TsOH)/toluene,^{7c} or pyridinium *p*-toluenesulfonate (PPTS)/acetic anhydride.¹¹ We found the PPTS approach affords clean product in a satisfactory yield by a simple filtration. Compound **5** is an orange/red solid, with a high melting point and excellent thermal and photochemical stability.

Scheme 1. Synthesis of Pentacenequinone **5**



A similar methodology allowed us to successfully synthesize two *para*-hexacenequinones (**10** and **11**) from the

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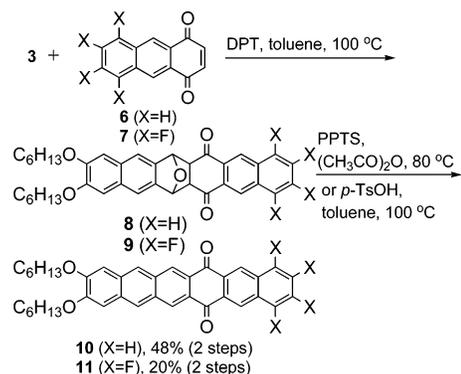
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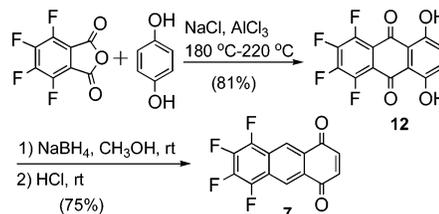
corresponding 1,4-anthraquinones (**6** and **7**) as the dienophiles (Scheme 2).

Scheme 2. Synthesis of Hexacenequinone **10** and **11**



Dienophile 6,7,8,9-tetrafluoro-1,4-anthraquinone (**7**) was synthesized previously from the oxidation of corresponding 1,4-dihydroquinone.¹² Here, we report a more convenient route, as shown in Scheme 3. A Friedel–Crafts biscycloacylation

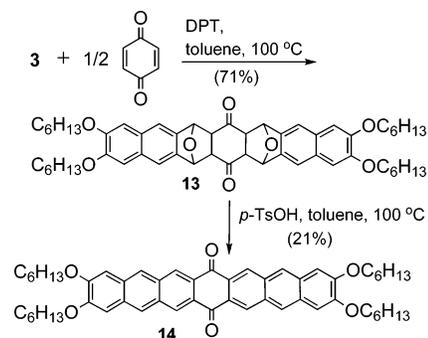
Scheme 3. Synthesis of Tetrafluoroanthraquinone **7**



of 1,4-dihydroxybenzene and 3,4,5,6-tetrafluorophthalic anhydride was conducted in a melt of aluminum chloride/sodium chloride (AlCl₃/NaCl) to give tetrafluoroquinizarin **12**.¹³ Reduction of **12** with sodium borohydride (NaBH₄) and a subsequent dehydration with concentrated aqueous HCl afforded **7** as a dark-brown solid.¹⁴

Using 1,4-benzoquinone as the limiting reagent, we prepared a tetraalkoxy-substituted heptacenequinone (**14**)

Scheme 4. Synthesis of Heptacenequinone **14**



(Scheme 4). Interestingly, the only detected products are exo/exo and exo/endo isomers of **13**. Dehydrating both isomers yields heptacenequinone **14** as a yellow/orange solid.

A solution of the acenequinones possesses a characteristic strong absorption band at 350–400 nm and a second absorption band at 420–500 nm (Figure 1A), both of which can be assigned as $^1(\pi, \pi^*)$ absorptions.¹⁵

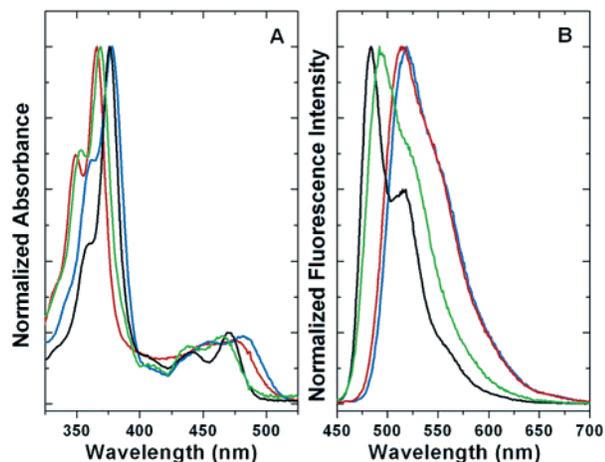


Figure 1. UV–vis absorption spectra and fluorescence spectra of acenequinones in toluene (**5**, red; **10**, green; **11**, blue; **14**, black).

When compared to their nonsubstituted hydrocarbon acene analogues, these acenequinone compounds have broadened absorption peaks that are red shifted by about 20–30 nm. These differences are the result of intramolecular charge transfer (ICT) character between the electron-withdrawing quinoid moiety and electron-donating alkoxy side chains.¹⁵

All the acenequinone derivatives are fluorescent in solution, with the relative quantum yields ranging from 0.18 to 0.30 (Table 1). Figure 1B displays the fluorescence spectra of the acenequinones in toluene. The fluorescence spectra reveal that the emission maximum (λ_{em}) of **10** has a 30 nm blue shift as compared to that of **5**. This blue shift results from the reduced ICT character of **10** because the naphtho-fused quinoid group has weaker electron-withdrawing properties than the benzo-fused quinoid group in **5**.^{5a} Such an effect was also demonstrated by the 35 nm red shift of the λ_{em} of **11** and the 10 nm blue shift of the λ_{em} of **14**, with respect to the λ_{em} of **10**. Clearly, the fluorine groups significantly enhance the ICT character in **11**.^{5d} These results show that photophysical properties of *para*-acenequinones can be tuned by attaching suitable functional groups.

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Table 1. Absorption and Emission Maxima and Quantum Yields of Acenequinones in Toluene

| compd | λ_{max} (nm) | λ_{em} (nm) | Φ_{rel}^a |
|-----------|----------------------|---------------------|----------------|
| 5 | 366 | 515 | 0.30 |
| | 475 | | |
| 10 | 369 | 493 | 0.21 |
| | 465 | | |
| 11 | 378 | 519 | 0.24 |
| | 482 | | |
| 14 | 376 | 484 | 0.18 |
| | 470 | | |

^a Fluorescence quantum yield relative to coumarin 153 ($\Phi_{rel} = 0.38$).

The orientation properties of acenequinone dyes in LC hosts were investigated via the measurement of polarized absorption and fluorescent spectra in aligned test cells. Samples were prepared by loading dye/LC fluids (0.1–0.5 wt % dye in MLC-6884) into LC test cells.¹⁶ The dye/LC mixture forms a homogeneously aligned structure, and the polarized UV–vis absorption and emission spectra were determined.

The polarized absorption spectra of acenequinone **5** in LC hosts are displayed in Figure 2A. The anisotropy of molecular

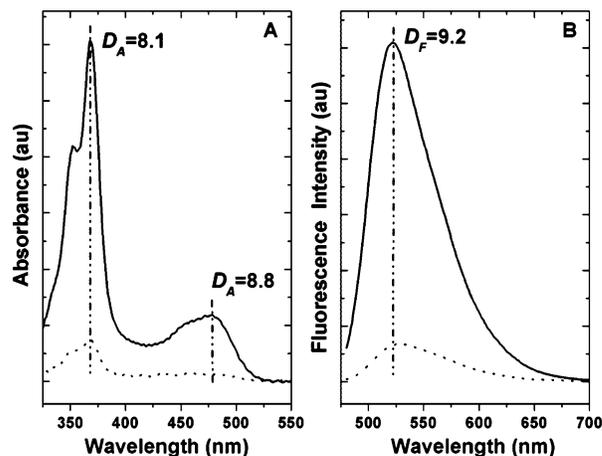


Figure 2. Polarized absorption (A) (solid line, $A_{||}$; dotted line, A_{\perp}) and fluorescence spectra (B) (solid line, $I_{||}$; dotted line, I_{\perp}) of **5** in MLC-6884. The vertical dotted-dashed lines indicate the wavelengths of dichroic ratios reported.

absorption transition moments is in agreement with our preliminary calculations that reveal the transitions of the two major absorption bands are aligned with the long molecular axis.¹⁷ Therefore, the dichroic ratio (D_A) and order parameter (S_A) of a dye in LC can be calculated by using the following equations:

(16) See Supporting Information for detailed descriptions of test cells and LCs.

(17) The computation was carried out by Gaussian, employing ZINDO on the DFT B3LYP 6–31.G(d) optimized geometry. See Supporting Information for details.

$$D_A = A_{\parallel}/A_{\perp}$$

$$S_A = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$$

where A_{\parallel} and A_{\perp} represent the absorbance for parallel and perpendicular irradiation with respect to the LC director.³ As summarized in Table 2, those compounds demonstrated

Table 2. Spectral Characterizations, Dichroic Ratios, and Order Parameters of Acenequinones in MLC-6884

| compd | λ_{\max} (nm) | D_A | S_A | λ_{em} (nm) | D_F | S_F |
|-----------|-----------------------|-----------------------|------------------------|----------------------------|----------------|----------------|
| 5 | 368 | 8.1 | 0.70 | 522 | 9.2 | 0.73 |
| | 478 | 8.8 | 0.72 | | | |
| 10 | 373 | 8.8 | 0.72 | 504 | 10.4 | 0.76 |
| | 470 | 9.6 | 0.74 | | | |
| 11 | 383 | 8.9 | 0.72 | 532 | 10.1 | 0.75 |
| | 485 | 10.0 | 0.75 | | | |
| 14 | 380 | 8.7–12.8 ^a | 0.72–0.80 ^a | – ^b | – ^b | – ^b |
| | 477 | 7.7–8.8 ^a | 0.69–0.72 ^a | | | |

^a The exact D_A and S_A of **14** could not be obtained due to the strong interference from the test cell. ^b The D_F and S_F of **14** could not be determined due to its low relative quantum yield and poor solubility in LCs.

dichroic ratios in the range of 8–10, indicating their excellent alignment in the LC host. It has been reported that dyes with a dichroic ratio greater than 8 are appropriate for practical use.^{5b}

Figure 2B shows the representative polarized fluorescence spectra. The dichroic ratio (D_F) and order parameter (S_F) based on polarized fluorescence can be calculated by using the following equations:

$$D_F = I_{\parallel}/I_{\perp}$$

$$S_F = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$$

where I_{\parallel} and I_{\perp} represent the emission intensity for parallel and perpendicular irradiation with respect to the LC director.¹⁸ Order parameter values from the polarized fluorescence are similar to those from the polarized absorption spectra (Table 2). Compounds **10** and **11** have higher aspect ratios and as expected have higher orientation properties than **5**. This feature agrees with the classic model that elongation of dichroic dye molecules should enhance their orientation in nematic LCs. The fluorescence maxima of acenequinones in LCs were found to have a small blue shift (7–13 nm) as compared to those in toluene solution. This feature is likely due to the different dielectric properties of each medium.

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The reorientation of dyes under the electric field was demonstrated in a test cell (Figure 3), containing a solution

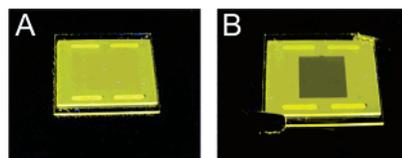


Figure 3. Fluorescent images of a test cell containing **5** in E7 (A, no applied voltage; B, 9 V applied voltage). The sample was excited with a 365 nm light from a hand-held UV lamp.

of 0.2 wt % **5** in E7 (a commercial LC mixture with positive dielectric anisotropy). Because the test cell is coated with parallel rubbed polyimide films, the LC/dye mixture forms a homogeneously aligned texture, with the long molecular axis of LCs and dyes parallel with the rubbing direction. Therefore, acenequinone dyes in this orientation give strong emission when they are excited by a UV light (Figure 3A). Upon application of an electric field, the LC director and acenequinone backbones align normal to the surface of the test cell. Consequently, the transition dipole of the dye compound is parallel to the direction of incident light, resulting in decreased projection of the transition dipole along the electric vector of incident UV light and minimal absorption and emission (Figure 3B).^{5c,19} The polarized fluorescence is rapidly recovered upon removal of the voltage.

In summary, we have reported a convenient synthesis of substituted *para*-acenequinones by employing DPT and an anthracene 1,4-endoxide. The polarized absorption and fluorescence results demonstrate that acenequinones align with nematic LC hosts, indicating their potential as dichroic dyes for GH-LCDs. In addition, the sensitivity of the emission to the substitution allows the tuning of fluorescence by functionalization of the acenequinone chromophore.

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Supporting Information Available: Experimental procedures and characterization data for new compounds reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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